



A review on exergy analysis of biomass based fuels

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ABSTRACT

Renewable energy sources can be a good substitute of the fossil fuels which are being terminated fast. Nowadays biomass and biofuels are considered because of their environment friendly characteristics and their ability of supplying much more energy. An alternative means to select the most efficient and convenient biomass, is exergy analysis. The present paper has reviewed the existent surveys on the exergy analysis of different kind of biomass included the woody biomass, herbaceous and agricultural biomass, aquatic biomass, contaminated biomass and industrial biomass. The most common thermochemical processes are investigated and the efficiency of the different process and various kinds of biomass are determined.

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1. Introduction

Fossil fuels, the largest resource of the world's energy demand, are being diminished fast. Based on the Kyoto protocol [1], replacing the fossil fuel which leads to global problems and greenhouse gas emission by the hydrogen energy system and biomass is essential [2]. Biofuels with the potential of supplying much more energy than the fossil fuel are known as the clean, renewable feedstock. Nowadays biofuels specially biodiesel are considered much more than before [3,4]. An alternative means to select the most convenient biomass, is exergy analysis. This thermodynamic analysis technique estimates the efficiency of the process and determines the energy quality and usefulness [5]. Exergy analysis makes us able to specify the maximum performance of a system and the sources

of the irreversibilities [6]. During the past decades exergy analysis had been used to evaluate the performance of different systems and to improve their efficiencies [7–12]. The relationship between the exergy analysis and the sustainability shows that diminution the loss of energy quality (exergy) leads to increment of the sustainability of energy use [13]. There are numerous studies on exergy analysis and the exergy destructions which were listed in Saidur et al. [14] article, precisely.

The exergy analysis of material streams can be divided to physical and chemical exergy rate. The physical exergy rate is due to the difference of the system condition and the reference condition. In some surveys the physical exergy of biomass was considered to be zero as the initial and final state was assumed to be same as the dead state [15,16]. There are some simplicities and assumption in calculating the chemical exergy of biomass. In some cases the chemical exergy of the exhaust gases and ash may be neglected [15,17,18]. The most prevalent correlation that had been used to calculate the chemical exergy of biomass, in case of knowing the

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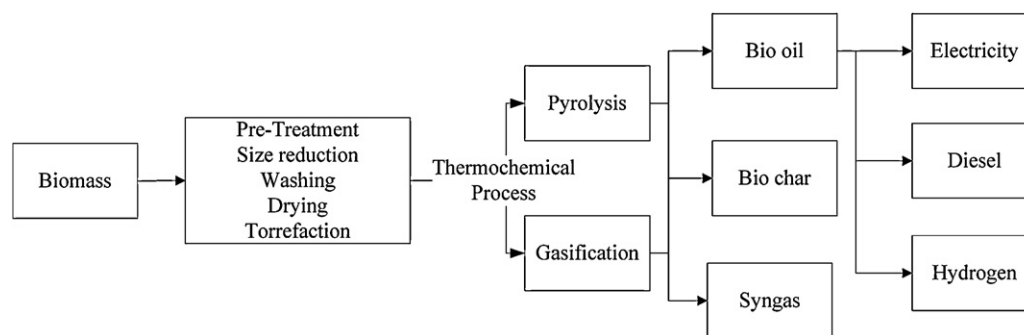


Fig. 1. Schematic of thermochemical processes of biomass [35].

chemical composition of them, is Szargut's correlation [19]. Besides the mentioned correlation, Hepbasli [20] reported that an equation can be used to evaluate the specific chemical exergy of biomass. In addition to the differences of the applied equation in the surveys, the considered method to calculate each term of these equations can affect the value of the chemical exergy. Chemical exergy is defined as the product of lower heating value (LHV) of the fuel and the exergy coefficient. The amount of LHV can be evaluated based on the higher heating value (HHV) [21]. HHV can be obtained from the existent data in literature or directly from the experimental correlations [22–24].

The present paper has reviewed the existent surveys on the exergy analysis of different kind of biomass. The articles are classified four main groups based on their studied biomass. The classification of biomass is based on the Vassilev et al.'s surveys [25]. It may be reported that to the best of authors' knowledge there is no work on the review of biomass as a fuel. Therefore, this review is expected to fill this gap.

2. General consideration of thermo-chemical conversion technologies of biomass

Biological and thermochemical processes are two main methods to convert the biomass into commercial products. Thermochemical converting method can be divided into three main groups of combustion, pyrolysis and gasification [26–28]. The desired form of energy and the type of biomass are two important factors that determine the conversion process.

Direct combustion of biomass is the traditional way of using biomass. Theoretically, it is possible to burn any type of biomass but the feasibility of biomass combustion was investigated by McKendry [29] and it was found that the combustion process is possible for the biomasses with moisture content of less than 50%.

Pyrolysis is heating biomass in absence of the air, and it changes the biomass into bio-oil, char and tar [26]. Demirbas [30] had defined the pyrolysis as a thermal destruction of organic materials in the absence of the oxygen.

One of the most effective converting methods for biomass is gasification, in which through a partial oxidation the biomass is converted into synthesis gas and condensable compounds [31,32]. During the gasification the chemical energy of the biomass changes into the thermal and chemical energy of the synthesis gas [33]. Gasification achieves a higher conversion rate in comparison with pyrolysis and combustion [34]. The thermochemical processes are described schematically in Fig. 1.

3. Studies conducted on exergy analysis of biomass

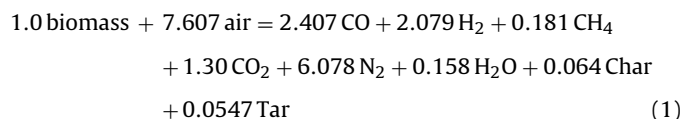
The exergy analysis of woody biomass will be reviewed first in Section 3.1 and then the exergy analysis of herbaceous and

agricultural biomass will be described in Section 3.2. The exergetic efficiency of aquatic biomass will be evaluated in Section 3.3 and finally the exergy analysis of contaminated biomass and industrial biomass will be presented in Section 3.4.

3.1. Exergy analysis of woody biomass

The exergy analysis of hydrothermal upgrading of biomass (HTU) process was carried out by Zhong et al. [36]. During the HTU, the biomass is converted to a liquid fuel with an approximately high energy, which is called biocrude. The ratio of the standard chemical exergy and net calorific value of wood was calculated based on the Szargut et al. formula [19], and they had found that maximum exergy efficiency of this process can be as high as 86%. By calculating the maximum exergy of the reactor effluent steam, it had been shown that it is higher than the minimum exergy which was needed for the process.

Rao et al. [37] conducted a survey on the mass, energy and exergy balance analysis of a counter current fixed-bed gasifier. The stoichiometric equation of the wood chips gasification is as follows:



where biomass = $\text{C}_{4.643}\text{H}_{6.019}\text{O}_{2.368}\text{N}_{0.021}$, char = $\text{C}_{6.750}\text{H}_{1.970}\text{O}_{1.042}\text{N}_{0.023}$ and tar = $\text{C}_{5.600}\text{H}_{6.930}\text{O}_{1.608}\text{N}_{0.005}$.

They calculated the exergy balance by combining the entropy and energy balances based on methods used by Kirillin et al. [38]. The exergy evaluation of the solid was done by using Shieh and Fan formula [39]:

$$E_{\text{xs}} = 4.1868\{8177.79[\text{C}] + 5.25[\text{N}] + 27,892[\text{H}] - 3173.66[\text{O}] + 0.15[\text{O}](7837.67[\text{C}] + 33888.89[\text{H}] - 4236.1[\text{O}])\} \quad (2)$$

The exergy of the mixture was calculated based on the Maxwell's thermodynamics relationships by assuming the negligible pressure variation and being ideal gas for the gas components [40]. The thermodynamic efficiencies were calculated in a similar way as the Chern et al. [41] had done and were evaluated in three different temperature of ambient and the lowest and highest temperatures of the wood chips during the gasification which are 25 °C, 293 °C, and 348 °C, respectively. The maximum second law efficiency of the wood chips was reported to be 65.5% which was related to the highest temperature of the process and in the case of considering all the product streams useful.

A comparison between gasification of torrefied wood and conventional gasification of wood was done by Prins et al. [42]. Wood torrefaction as a mild pyrolysis process was suggested to improve the wood properties, and it would lead to an increment in heating value

about 5–25%. During the torrefaction process, the volatile matter and moisture content of wood was decreased, compared to the original wood [43]. Considering the electricity required for cryogenic air separation, size reduction of torrefied wood and recycling cold synthesis gas for quenching the product gas of the gasifier, they defined the overall exergy efficiency as below:

$$\psi = \varepsilon_{\text{product gas}} + \varepsilon_{\text{steam}} - \frac{(E_{\text{air separation}} + E_{\text{size reduction}} + (E_{\text{gasification}} / \psi_{\text{electricity generation}}))}{\varepsilon_{\text{wood}}} \quad (3)$$

where ψ represents the overall efficiency, ε and E are shown the exergy and electricity, respectively.

Focusing on the gasification process, the chemical exergy of different type of biofuels was evaluated and the gasification efficiency of treated wood and untreated wood are compared [44]. The gasification model that was used comes with some assumption and simplification such as reaching the chemical equilibrium for gasifier products, ignoring the ashes and neglecting the heat losses of gasifier and dryer. The following correlation was used to calculate the exergy efficiency:

$$\psi = \frac{(\varepsilon_{\text{ch,gas}} + \varepsilon_{\text{ph,gas}})}{\varepsilon_{\text{ch,biomass}}} \quad (4)$$

Exergy evaluation is done based on the Szargut et al. correlations [19]:

$$\varepsilon_{\text{ch,total}} = Z_{\text{org}}(\beta \text{LHV}_{\text{org}}) + Z_s(\varepsilon_{\text{ch,s}} - C_s) + Z_{\text{water}}\varepsilon_{\text{ch,water}} + Z_{\text{ash}}\varepsilon_{\text{ch,ash}}$$

The factor β is the ratio of the chemical exergy to the LHV of the organic fraction of biomass, which was calculated based on the Szargut et al. equations [19] for the solid biofuels:

$$\beta_{\text{LHV}} = \frac{1.044 + 0.0160(Z_{\text{H}}/Z_{\text{C}}) - 0.3493(Z_{\text{O}}/Z_{\text{C}})[1 + 0.0531(Z_{\text{H}}/Z_{\text{C}})] + 0.0493(Z_{\text{N}}/Z_{\text{C}})}{1 - 0.4124(Z_{\text{O}}/Z_{\text{C}})} \quad (6)$$

The proximate and ultimate analysis data of treated wood and untreated wood were obtained from the Phyllis database [45]. The calculated β of the treated wood and untreated wood are approximately same which was 1.119 and 1.122, respectively. The reported chemical exergy was found to be 17,129 kJ/kg for treated wood and 16,634 kJ/kg for untreated wood. The efficiency based on the chemical and physical exergy of both of the fuels are around 75%.

Exergetic efficiency of the conversion process of biomass to synthetic natural gas (SNG) was evaluated by Juraščík et al. [46]. They had simulated the conversion process of woody stream with higher heating value of 19.7 MJ/kg by using the Flow sheeting program Aspen plus. The exergy balance analysis and irreversibility evaluation was done based on the Szargut et al. [19] calculation. They had considered three different definitions of exergy efficiency which are listed below:

$$\psi_1 = \frac{E_{\text{SNG}}}{E_{\text{tot,in}}} \quad (7)$$

Considering the exergy rate of the product steam streams:

$$\psi_2 = \frac{(E_{\text{SNG}} + E_{\text{steam,prod}})}{E_{\text{tot,in}}} \quad (8)$$

Considering the both exergy rate of steam streams and heat of the production:

$$\psi_3 = \frac{(E_{\text{SNG}} + E_{\text{steam,prod}} + E_{\text{heat,prod}})}{E_{\text{tot,in}}} \quad (9)$$

They had concluded that the higher gasification pressure can affect the ψ_1 , ψ_2 positively unlike the ψ_3 which increase at lower pressure. The lower heating value evaluation and the exergy content

calculation of biomass was done based on the work carried out by Channiwalwa et al. [47]. The obtained exergy efficiency of the computer model for different conditions was about 69.5–71.8%. Two case studies were investigated to validate the computer model of the process. One of the case studies was a quasi-equilibrium model [48] and another one was the case in which conversion process occurs incompletely. Exergy efficiency of the first case study was much more similar to the computer simulation than the second one. The results of second case study showed a reduction of 7–8% in exergy efficiency.

Evaluating the exergetic efficiency of the conversion process of biomass to SNG during an indirect gasification had been done by Vitasari et al. [49]. The effect of main process parameters such as the gasification pressure, methanation pressure and the temperature of the cooled reactor were investigated. By using the Gibbs-reactor model of Aspen Plus simulator both gasification and combustion section were modelled. However, based on the Jurascik et al. work, the gasification model does not affect the rate of produced SNG and the error of the exergetic efficiency is negligible [50]. Treated wood with the higher heating value of 19.69 was one of the biomass fuels which were considered. The ratio of the exergy output relative to the exergy input of the process was defined as the overall exergetic efficiency (ψ):

$$\psi = \frac{E_{\text{SNG}} + \sum_{\text{out}} E_{\text{stream}}}{\sum_{\text{in}} E_i + \sum_{\text{in}} E_j^Q + \sum_{\text{in}} E_k^W} \quad (10)$$

where all the exergy terms were calculated based on the Szargut and Rivero [51,52] correlations. The influence of the pressure and temperature on the exergy efficiency of the process was investigated by Vitasari et al. [49]. Increment of SNG production

rate and reduction of exergy input by increasing the gasification pressure had been shown as the two main causes of positive influence on the exergetic efficiency. The largest irreversibilities of using treated wood as feedstock were determined in biomass gasification, methanation section and CO₂ removal. Irreversibilities of gasifier which was about the half of the total irreversibilities of the process can be reduced with gasification pressure. Influence of temperature was investigated by keeping the pressure constant. Increasing the temperature in the first methanation reactor would lead to reduction of exergetic efficiency for treated wood.

Treated wood with high carbon and low ash content was considered as one of the best feedstock for producing SNG.

The exergy assessment of an integrated Rankine cycle with a biomass combustor was investigated by Al-Sulaiman et al. [53]. Pine sawdust with 10% moisture content was the biomass fuel which was considered as the fuel of combustor. The electrical-exergy efficiency of the system was defined as the rate of the net power to the exergy rate of the fuel. The exergy rate of the fuel can be evaluated by using Eq. (11) [54]:

$$E_{\text{xf}} = \beta \text{LHV}_f \quad (11)$$

The effect of the evaporator pinch point, pump and turbine inlet temperature on the exergy efficiency were investigated, and it was found out that the main sources of exergy destruction are the evaporator and biomass combustor.

The summary of reviewed articles in exergy analysis of woody biomass is tabulated in Table 1.

Table 1
Findings of exergy analysis of woody biomass.

No.	Thermochemical process	Type of woody biomass	Key results	Ref.
1	Hydrothermal upgrading of biomass	Wood	Maximum exergy efficiency of this process can be as high as 86%.	[25]
2	Gasification	Wood chips	The maximum second law efficiency of the wood chips is reported to be 65.5%.	[26]
3	Gasification	Torrefied wood	The overall efficiency of air-blown gasification is lower for torrefied wood than wood.	[31]
4	Gasification	Treated wood and untreated wood	The exergetic efficiency of both fuels are reported around 75%.	[33]
5	Gasification	Wood	The obtained exergy efficiency of the computer model is about 69.5–71.8%.	[35–47]
6	Indirect gasification	Treated wood	Largest irreversibilities occur in biomass gasification, methanation and CO ₂ removal.	[38]
7	Combustion	Pine sawdust	Main sources of exergy destruction are the evaporator and biomass combustor.	[42]

3.2. Exergy analysis of herbaceous and agricultural biomass

Based on the “process analysis method” the exergy of rape seed oil methyl ester (RME) was investigated by Kalinci et al. [17]. Process analysis method is a common method to obtain reasonable data for energy and exergy analysis [55,56]. The chemical exergy of liquid fuels were calculated based on Eq. (12) [19]:

$$E_{ch} = \beta(C + L_w Z_w) + E_{chw} Z_w \quad (12)$$

where C represents the net calorific value, the enthalpy of phase change for water was shown by L_w which was equal to 2440 kJ/kg and chemical exergy of water (E_{chw}) was 50 kJ/kg. The quality factor (β) can be estimated by following correlation (13):

$$\beta = \frac{1.041 + 0.216(Z_{H_2}/Z_C) - 0.250(Z_{O_2}/Z_C)[1 + 0.788(Z_{H_2}/Z_C)] + 0.045(Z_{H_2}/Z_C)}{1 - 0.304(Z_{O_2}/Z_C)} \quad (13)$$

The calculated exergy of rape seed was reported to be 28.7 MJ/kg, where the estimated chemical exergy of rape seed oil and RME was reported to be 44.8 MJ/kg and 50.5 MJ/kg, respectively.

Exergy analysis and sustainability of the ethanol production from lignocellulosic biomass were evaluated by Ojeda et al. [18]. They had considered three different technologies for converting the sugarcane bagasse to the ethanol. Exergy was calculated for the main stream of the process such as re-treatment, fermentation and separation. The exergy balance for each step of the process had been written as:

$$\begin{aligned} &\text{Exergy input} - \text{Exergy output} - \text{Exergy consumption} \\ &= \text{Exergy accumulation} \end{aligned} \quad (14)$$

The consumed exergy was estimated according to Shukuya et al. [57] correlation. The exergetic efficiency of the process was calculated based on Eq. (15):

$$\text{efficiency} = \frac{\text{effective exergy obtained}}{\text{exergy consumed in resource}} \quad (15)$$

The highest efficiency was reported in case of steam explosion pre-treatment which is 79.58% and the lowest one (73.98%) was related to acid diluted pre-treatment.

The effective method that Ojeda et al. [58] had used to evaluate the efficiency of converting lignocellulosic biomass to bioethanol by means of enzymatic hydrolysis reactor, was exergy analysis. Kinetic [59] and reactor models were investigated in their survey. Exergy flows of the streams were calculated by means of Gibbs free energy formation [60] and the exergy efficiency was obtained based on Eq. (16):

$$\eta_e = \frac{\text{Exergy in products}}{\text{Total exergy input}} \quad (16)$$

The reported exergy efficiency for continuous stirred-tank reactor was between 64.27% and 68.12% and this value changes to

65.21–72.06% for the plug-flow reactor. The effect of the operation temperature on the exergetic efficiency was also studied and they have found that for both types of reactors, increasing the operating temperature between 40 °C and 50 °C leads to an increment of exergetic efficiencies.

Applying the combustion diagnosis model, Benjumea et al. [15] had evaluated the effect of palm oil fuelling and the altitude on the performance of the diesel engine. The considered model was based on the Lapuerta et al. [61]. The defined dead state was a pressure of 101.325 kPa and the temperature of 298.15 K. According to the Rosen et al. [62,63], they assumed the same dead state for different altitudes. The exergy destruction was calculated based on Eq. (17):

$$\delta E_d = - \left(1 - \frac{T_o}{T} \right) \delta Q_w - (P - P_o) dV - m_{cyl} de_{cyl} + e_f^{ch} dm_f \quad (17)$$

The chemical exergy of the fuel (e_f^{ch}) was obtained due to its composition and LHV [64]. In calculating the exergy destruction, the chemical exergy of exhausted gases was not considered. The result of this survey had shown that, increasing the altitude leads to a reduction of the exergy destruction. They had also pointed out that variation of chemical composition and burning rate of the fuel would affect the exergy destruction.

The performance of compression engine using the cotton seed oil and palm oil as biofuels, were evaluated by Azoumah et al. [65]. The correlation that they had considered for the exergy consumption is:

$$E_X = \dot{W} + \delta E_X \quad (18)$$

where the exergy destroyed (δE_X) was calculated based on the Gouy–Stodola theorem, and the chemical exergy of the fuel was not considered in this survey. The exergy efficiency was defined as the ratio of converted electric power to the exergy consumption. The result had shown that as engine load increases, the exergy efficiency would decrease.

Renewability of the corn-ethanol process was studied by Yang et al. [66] by means of the cumulative exergetic method [67]. The net exergy consumption was evaluated based on Eq. (19) [68,69]:

$$CHE_X = CE_X C - E_{xp} \quad (19)$$

where CNE_X and $CE_X C$ represent the concept of net exergy consumption and cumulative exergy consumption, respectively. The E_{xp} determines the chemical exergy of products. The total CNE_X was obtained to be 259,540 MJ.

The reviewed papers in herbaceous and agricultural biomass are summarized in Table 2.

Table 2

Summary of results on exergy analysis of herbaceous biomass.

No	Process	Type of woody biomass	Key results	Ref
1	RME production	Rape seed oil	The calculated chemical exergy of rape seed oil and RME is 44.8 MJ/kg and 50.5 MJ/kg, respectively.	[7–17]
2	Ethanol production	Lignocellulosic	Highest efficiency is reported 79.58% whereas the lowest efficiency is 73.98%.	[8–18]
3	Bioethanol production	Lignocellulosic	The reported exergy efficiency for continues stirred tank is in range of 64.27–68.12% and it changes to 65.21–72.06% for plug flow reactor.	[47]
4	Combustion in diesel engine	Palm oil	The result has shown that increasing the altitudes lead to a reduction of exergy destruction.	[5]
5	Combustion in an engine	Cotton seed oil, palm oil	The results pointed out that as engine loads increases the exergy efficiency would decrease.	[54]
6	Ethanol production	Corn	The obtained net exergy consumption for the whole process is 259,540 MJ.	[55]

3.3. Exergy analysis of aquatic biomass

Exergetic efficiency of the algal biodiesel production process was assessed by Sorguven et al. [70]. The exergy balance around the mixer, reactor, holding tank and separation tank was calculated by the authors. The chemical exergy of C_2H_4 was predicted with the aid using Eq. (20) [71]:

$$e^{ch} = LHV \left(1.04224 + 0.011925 \frac{y}{z} - \frac{0.042}{z} \right) \quad (20)$$

Exergy destruction was presented as a function of diesel cycle parameters such as heat input, cut off ratio and compression ratio:

$$X_{destroyed} = Q_{in} \frac{1}{k(r_c - 1)r_c^{k-1}} (r_c^k - k \ln r_c - 1) \quad (21)$$

Considering $r = 15$, $r_c = 5$ and $k = 1.4$, therefore exergy destruction was equal to $0.38 \times Q_{in}$.

The total exergy loss of the process was calculated 0.19 GJ per ton of biodiesel and the reactor was detected as the main source of irreversibilities. Based on the Talens et al. work's [72] the actual exergy loss must be larger than the calculated value. Comparing the chemical exergy of the proposed biodiesel and other fuels, Sorguven et al. [70] had shown that, common diesel fuel had the highest exergy of 47.2 GJ/ton, which was followed by gasoline and algal biodiesel with chemical exergy of 46.9 GJ/ton and 40.1 GJ/ton, respectively.

3.4. Exergy analysis of contaminated and industrial biomass

The possibility of sludge gasification and methanol synthesis was assessed by Ptasiński et al. [73]. The process of synthesis methanol from sludge was simulated using the Aspen Plus and the exergetic efficiency of the process was demonstrated. The assumed LHV of the sludge was considered as 12 MJ/kg. Exergy analysis was carried out for the thermal dryer, gas cleaning segment, compressors, methanol synthesis and separation segments and heat recovery sections. The calculated chemical exergy of the sludge based on the Szargut et al. formula [19], was 2845 kJ/kg of wet sludge. Ptasiński et al. [73] had shown that the total irreversibilities increased with an increment in gasifier temperature and dry solid content. The highest exergy losses occurred in gasification segment, compression and thermal drying sections.

Five different conversion processes resulted in SNG, methanol, Fischer–Tropsch fuels, hydrogen and heat-electricity of several biowaste streams were evaluated in a survey by Sues et al. [34]. All the processes had been modelled in Aspen Plus to analyze the mass and energy balances. Kotas definition's [64] for exergy efficiency was selected to calculate the efficiency of the conversion process. The defined rational efficiency was shown in Eq. (22):

$$\psi_{ex} = \frac{E_{biofuels} + W_{out} + E_{surplus\ stream}}{E_{biomass} + E_{utilities} + W_{in}E_{in}^0} \quad (22)$$

Special chemical exergy of the compounds was obtained from the literature review [19]. Because of the effects of external heat,

three cases were considered in this study. It had been shown that the SNG production is the most efficient process among the five studied processes. The obtained exergetic efficiency of the SNG was ranged between 50 and 58%, whereas it was 45–52% for hydrogen production. They had also found that the most part of the irreversibilities occur in the gasifier.

4. Future direction

It seems that there is a lack of data on analysis of contaminated and industrial biomass, which is very important with respect to the environmental pollution. An exergy analysis of this sort of biomass can determine the importance and essentiality of their use.

An exergy analysis of other kind of thermochemical process rather than gasification could be a good research area for further studies.

5. Conclusion

Following conclusions can be made based on this study:

- (1) In most of the exergy analysis that had been done, gasification found to be the main thermochemical process. As it mentioned, gasification is the most effective converting method of biomass.
- (2) The calculated exergy efficiency and the exergy destruction were highly depended on the used procedures, equations and formulas.
- (3) Gasification, methanation and CO_2 removal are determined as the main sources of exergy losses.
- (4) Among the investigated feedstock for biodiesel production, which were cotton seed oil, rape seed oil and palm oil, palm oil has a good potential to be converted into a appropriate biofuel.
- (5) It has been shown that the chemical exergy of the algal biodiesel is close to the exergy of the common diesel fuel and gasoline, and by some improvements it may be a good choice.
- (6) Among the five different conversion processes resulted in SNG, methanol, Fischer–Tropsch fuels, hydrogen and heat-electricity of several biowaste streams, the exergy efficiency of the SNG production is the highest.
- (7) In most of the studies, Aspen Plus was used to simulate the process and analyze the mass and energy balances.

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